One-step reforming of CO_2 and CH_4 to high-value liquid chemicals and fuels at room temperature via plasma-driven catalysis

L. Wang,[a] Y. H. Yi,[b] C. F. Wu,[c] H. C. Guo,[b] and X. Tu*[a]

Abstract: Conversion of CO_2 with CH_4 into liquid fuels and chemicals in a single-step catalytic process bypassing the production of syngas remains a challenge. In this study, one-step synthesis of liquid fuels and chemicals (e.g. acetic acid, methanol, ethanol and formaldehyde) from CO_2 and CH_4 has been achieved at room temperature (30 °C) and atmospheric pressure for the first time using a novel plasma reactor with a water electrode. The total selectivity to oxygenates was ca. 50-60%, with acetic acid the major component at 40.2% selectivity, the highest value reported for acetic acid so far. Interestingly, direct plasma synthesis of acetic acid from CH_4 and CO_2 is an ideal reaction with a 100% atom economy, but it is almost impossible via thermal catalysis due to the significant thermodynamic barrier. The combination of plasma and catalyst in this process shows great potential for manipulating the distribution of different liquid chemicals.

Chemical transformation of CO_2 into value-added chemicals and fuels has been regarded as a key element of creating a sustainable low-carbon economy in the chemical and energy industry. A particularly significant route currently being developed for CO_2 utilization is catalytic CO_2 hydrogenation. This can produce a range of fuels and chemicals including CO, formic acid, methanol, hydrocarbons and alcohols; however, high H_2 consumption ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) and high operating pressure (~30-300 bar) are major challenges facing this process.

Instead of using H_2, direct conversion of CO_2 with CH_4 (dry reforming of methane, DRM) to liquid fuels and chemicals (e.g. acetic acid) represents another promising route for both CO_2 valorisation and CH_4 activation. CH_4 is an ideal H-supplier to replace H_2 in CO_2 hydrogenation as CH_4 has a high H density and is available from a range of sources (e.g. natural gas, shale gas, biogas and flared gas). Moreover, it is a cheap carbon source which can increase the atom utilization of CO_2 hydrogenation due to the stoichiometric ratio of C and O atoms, as well as reducing the formation of water.

Recently, Ge et al. investigated the direct C-C coupling of CO_2 and CH_4 to form acetic acid on a Zn-doped ceria catalyst using density functional theory (DFT) modeling [1]; this is an attractive route as direct converting of CO_2 and CH_4 to acetic acid is a reaction with 100% atom economy (R1). However, this reaction is thermodynamically unfavorable under practical conditions. The conventional indirect catalytic process often proceeds through two steps (Scheme 1): (1) DRM to produce syngas (CO and H_2) at high temperatures (> 700 °C); (2) conversion of syngas to liquid fuels and chemicals at high pressures. Such an indirect route for CO_2 valorisation and CH_4 activation is inefficient as the DRM process for syngas production is highly endothermic and requires high temperatures and energy input (R2). Catalyst deactivation due to carbon deposition is another challenge limiting the use of this reaction on a commercial scale. It is almost impossible to directly convert two stable and inert molecules (CO_2 and CH_4) into liquid fuels or chemicals in a one-step catalytic process bypassing the production of syngas. A step-wise method was proposed to convert CO_2 and CH_4 into acetic acid over Cu/Co-based catalysts [2], Pd/C, Pt/Al_2O_3 [3], Pd/SiO_2 and Rh/SiO_2 [4] via heterogeneous catalysis. The catalyst was first exposed to CH_4, forming CH_x species on the catalyst surface. Subsequently, the feed gas was changed from CH_4 to CO_2, forming acetic acid through the reaction of CO_2 with CH_x over the catalyst. This indirect process was complicated as a periodic change of reactant and collection of products was required [5].

$$CO_2 + CH_4 \rightarrow CH_3COOH,\ \Delta G_{298\,K} = 71.17\ kJ/mol \quad (R1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2,\ \Delta H_{298\,K} = 247\ kJ/mol \quad (R2)$$

Non-thermal plasma (NTP) offers a unique way to enable thermodynamically unfavorable chemical reactions to occur at low temperatures due to its non-equilibrium character: the overall gas temperature in a NTP remains low, while the generated electrons are highly energetic with a typical electron temperature of 1-10 e; sufficient to activate inert molecules (e.g. CO_2 and CH_4) into reactive species, including radicals, excited atoms, molecules and ions. These energetic species are capable of initiating a variety of chemical reactions. Although much effort has been expended on the use of NTP for the destruction of gas pollutants, far less has been done in regard to their use in the synthesis of fuels and chemicals [6]. Previous works on DRM using NTP mainly focused on syngas production [7], while very limited efforts have been devoted to this challenging reaction – one-step conversion of CH_4 and CO_2 to liquid fuels and chemicals [8]-[9]. A few groups reported the formation of trace oxygenates (e.g., alcohols and acids) as by-products in plasma DRM for syngas production [10]. So far, the use of NTP for the direct conversion of CO_2 and CH_4 into oxygenates has shown poor selectivity and yield.

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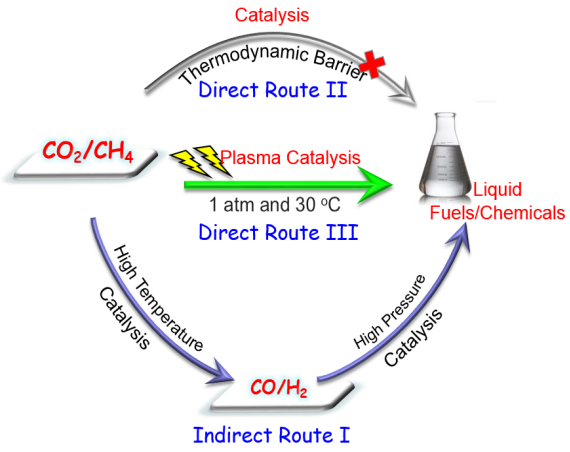


Scheme 1. Direct and in-direct processes for the conversion of CO_2 and CH_4 to liquid fuels and chemicals.

In this work, a novel dielectric barrier discharge (DBD) reactor with a ground water electrode (Schemes S1 and S2) has been developed for one-step conversion of CO_2 and CH_4 to oxygenates at room temperature (30 °C) and atmospheric pressure. This setup is unique and has not before been reported. Figure 1 shows that no reaction occurred in the 'catalyst-alone' mode at 30 °C without plasma. However, the use of a NTP enables this thermodynamically unfavorable reaction to occur at room temperature and produces liquid chemicals including acetic acid, methanol, ethanol and acetone, with acetic acid being the major product. Trace amounts of formic acid, propanol and butanol were also detected in the condensed liquid. In the plasma process without a catalyst ('plasma-alone'), a total liquid selectivity of 59.1% was achieved with 33.7%, 11.9%, 11.9% and 1.6% for acetic acid, ethanol, methanol and acetone, respectively (Figure 1a). The CO selectivity was limited at ca. 20.0% (Figure 1b), together with CH_4 and CO_2 conversions of 18.3 % and 15.4 %, respectively (Figure 1c).

Coupling the plasma process with a catalyst shows great potential to manipulate the production of different oxygenates at ambient conditions. Clearly, packing the Cu/γ-Al_2O_3 catalyst in the DBD enhanced the selectivity of acetic acid to 40.2%, compared to the 'plasma-alone' mode and the plasma reaction using γ-Al_2O_3 only (20.2%). Acetic acid was the major product regardless of the catalyst used, followed by methanol and ethanol (Figure 1a). Note HCHO was formed only when using the supported noble metal catalysts in the plasma reaction and the Pt/γ-Al_2O_3 catalyst showed the highest selectivity to HCHO. Compared to the 'plasma-alone' mode, placing the catalysts in the DBD showed similar gaseous products, with H_2, CO and C_2H_6 being the major gas products (Figure 1b). However, coupling the NTP with the catalysts enhanced the H_2 selectivity by 10-20% (except for Cu/γ-Al_2O_3), and slightly increased C_2H_6 production, but had a weak effect on CO selectivity (except Cu/γ-Al_2O_3 which decreased CO selectivity to 13.5%) and other C_xH_y (i.e., C_2H_2, C_2H_4, C_2H_6, C_3H_8 and n-C_4H_{10}). In addition, compared to the 'plasma-alone' mode, the conversion of CO_2 and CH_4 slightly decreased with packing catalysts. This phenomenon can be attributed to the change in discharge behavior induced by the catalyst, which had a negative effect on the reaction (Figure S1). Interestingly, acetic acid, hydroxyl-, ethyl ester was found on the reactor inner wall in the plasma-catalyst coupling mode. (Figure S2). These findings demonstrate the feasibility of using NTP for the direct conversion of CH_4 and CO_2 into higher value liquid fuels and chemicals in a single step process at ambient conditions, bypassing the formation of syngas.

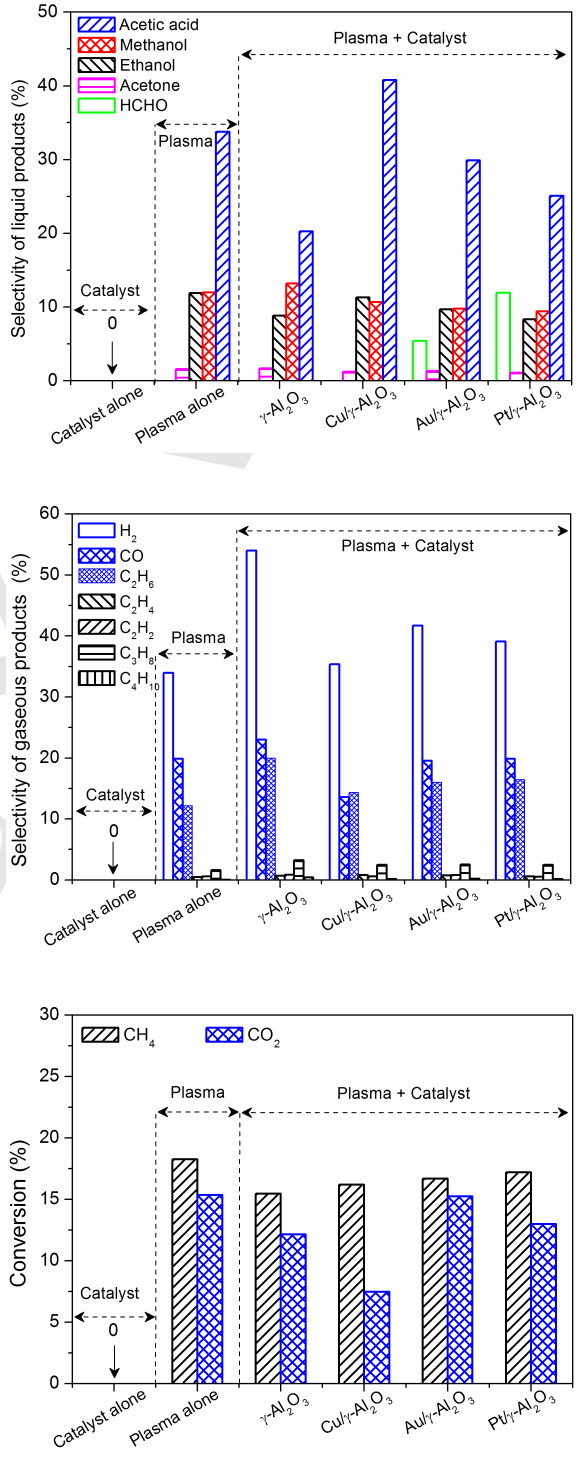


Figure 1. Effect of operating modes and catalysts on the reaction: (a) selectivity of oxygenates, (b) selectivity of gas products, (c) the conversion of CH_4 and CO_2 (total flow rate 40 ml/min, discharge power 10 W, catalyst ca. 2 g).

To understand the formation pathways of acetic acid, ethanol and methanol, optical emission spectroscopy (OES) diagnostics was used to investigate the species produced in the CH_4/CO_2 DBD (Figure 2). Reactive species, including CH, H_α, O radical, C_2, CO_2^+, CO_2, and CO Angstrom band, were identified, with CO, CH and H being the major species (Table S2).

CO is mainly derived from reaction S1-S3 (table S3) in the DBD. Our simulation showed electron impact CO_2 reactions produced ~95% vibrational excited CO_2 ($CO_{2(V)}$) compared to electronically excited CO_2 ($CO_{2(E)}$), as shown in Figure S3 and table S4. O radicals generated from CO_2 dissociation can attack $CO_{2(V)}$ molecules to produce CO (S1-S2) [11]. Different from CH, CH_3-derived from CH_4 dissociation cannot be detected using OES, but recent simulation revealed that electron impact dissociation of CH_4 leads to 79% CH_3 formation, whereas only 15% and 5% CH_2 and CH formation, respectively [12]. Therefore, CH_3 is the dominant specie in the CH_4/CO_2 DBD. In addition to electrons (S4 in table S3), reactive species such as OH, O and H can also react with CH_4 to produce CH_3 radicals (S5-S7) in the CH_4/CO_2 DBD. Additionally, OH is an important specie, especially for alcohol formation. In the CH_4/CO_2 DBD, OH could be produced indirectly via reaction S8-S13, with S8 and S9 the major channels based on the reaction rate coefficient and E_a [13]. Special attention was given to S10, although a very low reaction rate coefficient of 1.4E-29 and a high E_a of 111 kJ/mol were observed for ground state CO_2 reacting with H radical to produce OH radical, this reaction (S10) can be accelerated by $CO_{2(V)}$ instead of ground state CO_2 [14] and the vibrational energy of the reagents is the most effective in overcoming the activation barrier of the endothermic reaction [14-15]. Thus, the reaction $CO_{2(V)} + H \rightarrow CO + OH$ could be one of the major routes for OH formation in this study, as CO_2 mainly existed in vibrationally exited states (Figure S3).

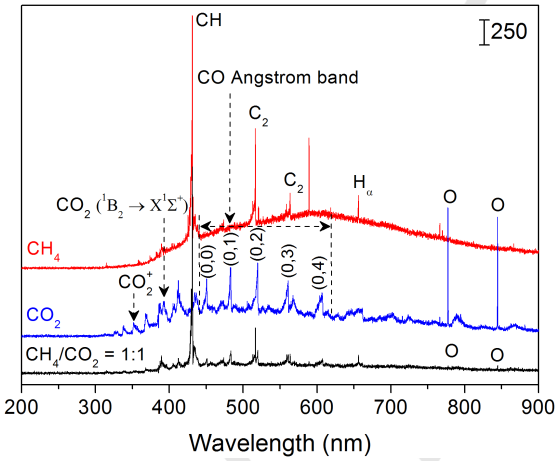
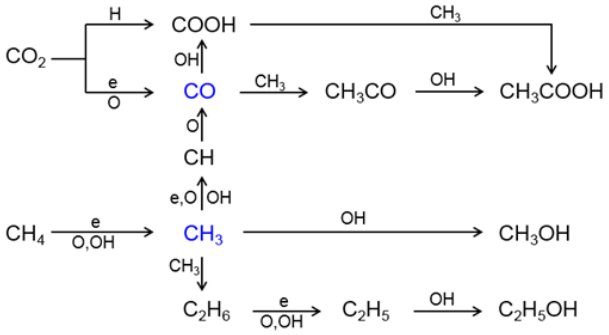


Figure 2. Optical emission spectra of CH_4, CO_2 and CH_4/CO_2 plasmas (total flow rate 40 ml/min, CH_4/CO_2 ratio 1:1, discharge power 10 W, 2 s exposure time).

Based on the analysis of gas and condensed liquid products combined with the OES, CO, CH_3 and OH radicals were the key species in the CH_4/CO_2 plasma reaction. Therefore, the possible reaction pathways for the formation of acetic acid, methanol and ethanol in this study are proposed in Scheme 2.

Acetic acid formation: Two possible reaction pathways could contribute to the formation of acetic acid. CO can react with a CH_3 radical to form an acetyl radical (CH_3CO) via reaction S14 in table S3 with a low energy barrier of 28.77 kJ/mol [16], followed by the recombination with OH to produce acetic acid via reaction S15 with no energy barrier [10g], which was further confirmed by Figures 3 and S4. Clearly, the selectivity of acetic acid increased initially, then decreased with the CH_4/CO_2 ratio, with the optimal acetic acid formation at a CH_4/CO_2 ratio of 1:1. Correspondingly, the relative intensity of the CO band and O atomic line increased with decreasing CH_4/CO_2 ratio from 3:1 to 1:2, while that of CH band had a reverse evolution character (Figure S4). This suggests that decreasing the CH_4/CO_2 mole ratio decreased the generation of CH_3 radicals, but increased OH formation. A similar mechanism of acetic acid formation was proposed using DFT modeling [10g] and by Eliasson et al. [10i]. In addition, direct coupling of CH_3 and carboxyl radicals (COOH) could also form acetic acid via reaction S16, while COOH radicals may be formed from reaction S17 and S18 in table S3 [10g].



Scheme 2. Possible reaction pathways for the formation of CH_3COOH, CH_3OH and C_2H_5OH in direct reforming of CH_4 and CO_2 using DBD.

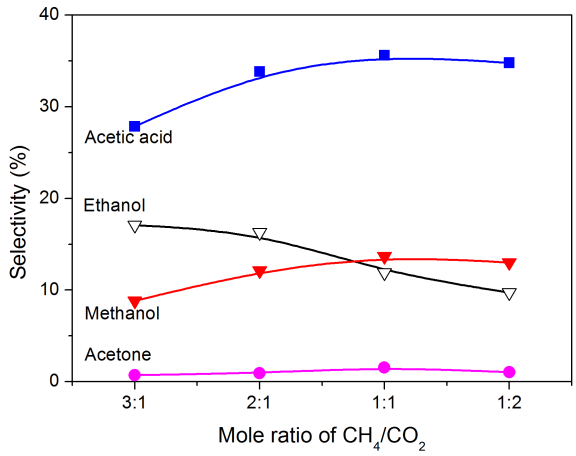


Figure 3. Effect of CH_4/CO_2 mole ratio on the selectivity of oxygenates without a catalyst (total flow rate 40 ml/min, discharge power 10 W).

Alcohol formation: Decreasing the CH_4/CO_2 ratio decreased the generation of CH_3 radicals, but increased OH formation (Figure S4). Simultaneously, the formation of CH_3OH increased initially with decreasing CH_4/CO_2 ratio and reached a peak at a CH_4/CO_2 ratio of 1:1. By contrast, the formation of C_2H_5OH decreased continuously as the CH_4/CO_2 ratio decreased (Figure

3). These findings suggest that the production of CH_3OH mainly depends on the generation of both CH_3 and OH radicals, while the formation of C_2H_5OH was more sensitive to the presence of CH_3 radicals in the plasma reaction as C_2H_5OH formation requires twice the amount of CH_3 radicals in comparison to the formation of CH_3OH. As shown in Scheme 2, CH_3OH can be directly formed from the coupling of CH_3 and OH radicals with a high rate coefficient (S19 in table S3) [17], while C_2H_5OH formation required several elementary reactions (S20-S24). The recombination of CH_3 radical with itself forms C_2H_6 (S20) [18], followed by dehydrogenation to form C_2H_5 radical via reaction S21-S23, with S21 as the primary reaction according to reaction rates [13d, 19]. C_2H_5 radical was eventually attached by OH to form C_2H_5OH at a high rate coefficient of 9.34E-11 cm^3 $molecule^{-1}$ s^{-1} (S24) [20].

Clearly, placing the catalysts in the plasma reaction can tune the distribution of oxygenates, especially for the formation of HCHO after packing the Pt and Au catalysts, revealing the occurrence of surface reactions in addition to the plasma gas phase reactions [21]. In traditional catalysis, CO hydrogenation, CH_3OH oxidation and methylene (CH_2) oxidation could form HCHO over noble-metal catalysts [22]. In this plasma process, packing noble-metal catalysts in the plasma had almost no influence on the CO selectivity, but decreased the selectivity of CH_3OH, C_2H_5OH and CH_3COOH and increased the selectivity of HCHO and C_2H_6 (Figure 1a). Considering the major species that existed in the CH_4/CO_2 DBD, CH_x (x = 4, 3, and 2) could be the primary source for HCHO formation via oxidation reactions. Namely, CH_x in the gas phase could be adsorbed onto the surface of the catalyst to form HCHO via the oxidation of $CH_{2,\,ad}$ ($CH_{x,\,ad}$ + O, H, OH → $CH_{2,\,ad}$), and to produce C_2H_6 via self-recombination of CH_3 radical instead of converting CH_3 to CH_3OH, C_2H_5OH and CH_3COOH. This could explain why the presence of the Au and Pt catalysts in the plasma decreased the formation of CH_3OH, C_2H_5OH and CH_3COOH, but enhanced the production of C_2H_6 and HCHO (Figures 1a and 1b). The possible pathways for the formation of major oxygenates on the catalyst surface were proposed in Scheme S3. In addition, a range of catalyst characterization (Figures S5-S8) suggest that metal particle size and interaction of metal and support are not the determining factors for the different reaction performances (Figure 1), whereas the bonding strength of adsorbed intermediates to the catalyst surface, i.e. oxygen adsorption energy (ΔE_O), could be a good activity descriptor towards the formation of different products in CO_2 hydrogenation [23].

In conclusion, one-step room temperature synthesis of liquid fuels and chemicals from the direct reforming of CO_2 with CH_4 has been achieved using a novel atmospheric pressure DBD reactor. The total selectivity of liquid chemicals was ca. 50-60%, with acetic acid the major product. The CH_4/CO_2 mole ratio and type of catalyst can be used to manipulate the production of different oxygenates. These results clearly show that non-thermal plasma can overcome the thermodynamic barrier to enable the direct transformation of CH_4 and CO_2 into a range of strategically important platform chemicals, especially the production of acetic acid with a 100% atom economy. Additionally, the coupling of the DBD with noble-metal catalysts produced formaldehyde which cannot be generated in the same plasma reaction without a catalyst. This finding suggests that new research should be directed at designing a catalyst with high selectivity towards a desirable product.

Acknowledgements

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Keywords: CO_2 conversion • CH_4 activation • non-thermal plasma • dry reforming • liquid fuels and chemicals

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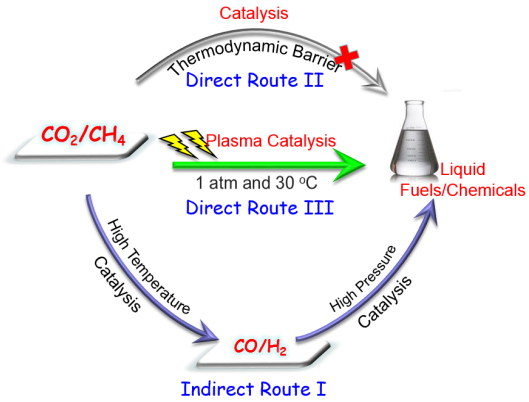
Entry for the Table of Contents

Layout 1:

COMMUNICATION

Single-step synthesis of liquid fuels and chemicals from CO_2 and CH_4 at ambient conditions was achieved using plasma-driven catalysis.



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One-step reforming of CO_2 and CH_4 to high-value liquid chemicals and fuels at room temperature via plasma-driven catalysis